

A11102 129282

NAT'L INST OF STANDARDS & TECH R.I.C.



A11102129282

/Scientific papers of the Bureau of Stan
QC1 .U572 V16;1920 C.1 NBS-PUB-C 1919

DEPARTMENT OF COMMERCE

SCIENTIFIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 400

IONIZATION AND RESONANCE POTENTIALS OF
SOME NONMETALLIC ELEMENTS

BY

F. L. MOHLER, Associate Physicist
PAUL D. FOOTE, Physicist

Bureau of Standards

OCTOBER 14, 1920



PRICE, 5 CENTS

Sold only by the Superintendent of Documents, Government Printing Office
Washington, D. C.

WASHINGTON
GOVERNMENT PRINTING OFFICE

1920

DEPARTMENT OF COMMERCE

SCIENTIFIC PAPERS

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 400

IONIZATION AND RESONANCE POTENTIALS OF
SOME NONMETALLIC ELEMENTS

BY

F. L. MOHLER, Associate Physicist
PAUL D. FOOTE, Physicist

Bureau of Standards

OCTOBER 14, 1920



PRICE, 5 CENTS

For sale by the Superintendent of Documents, Government Printing Office
Washington, D. C.

WASHINGTON
GOVERNMENT PRINTING OFFICE
1920

IONIZATION AND RESONANCE POTENTIALS OF SOME NONMETALLIC ELEMENTS

By F. L. Mohler and Paul D. Foote

CONTENTS

| | Page |
|------------------------------------------------------------------------------|------|
| I. Introduction | 669 |
| II. Methods of measurement | 671 |
| III. Measurements in the vapors of phosphorus, iodine, and sulphur | 673 |
| 1. Phosphorus | 674 |
| 2. Iodine | 676 |
| 3. Sulphur | 678 |
| IV. Spectral relations | 679 |
| V. Measurements in the common gases | 680 |
| 1. Introduction | 680 |
| 2. Nitrogen | 681 |
| 3. Oxygen | 683 |
| 4. Hydrogen | 685 |
| VI. Conclusion | 690 |

I. INTRODUCTION

The methods previously applied by the authors to the study of critical potentials in the metallic vapors have been, with some modifications, used for the elements phosphorus, iodine, sulphur, nitrogen, oxygen, and hydrogen. A study of the phenomena of electron currents in these polyatomic, nonmetallic elements can be best introduced by a statement of the essential features of electron impacts with metallic vapors, since work with these has yielded results of considerable accuracy and of a definite theoretical significance.¹

Collisions of low-speed electrons with metallic molecules are elastic, but with higher speeds two types of inelastic impact occur. (1) When the velocity in volts is greater than the resonance potential, collisions are inelastic and the velocity lost at collision is equal to the resonance potential V_r . The corresponding energy V_re is radiated as light of a single frequency ν related to V_r by the

¹ Franck and Hertz, *Verh. Deut. Phys. Ges.*, **16**, pp. 457 and 512, 1914. Tate and Foote, *J. Wash. Acad. Sci.*, **7**, p. 517, 1917; *B. S. Sci. Papers*, No. 317. *Phil. Mag.*, **26**, p. 64, 1918. Foote and Mohler, *Phil. Mag.*, **37**, p. 33, 1919; *J. Wash. Acad. Sci.*, **8**, p. 513, 1918. Foote, Rognley and Mohler, *Phys. Rev.*, **13**, p. 59, 1919. Mohler, Foote, and Stimson, *B. S. Sci. Papers*, No. 368. Foote and Meggers, *B. S. Sci. Papers*, No. 386. Abstracts of parts of the present paper have appeared in *Opt. Soc. Am. J.*, **4**, p. 49, 1920, and *Phys. Rev.*, **15**, p. 321, 1920.

quantum relation $V_1 e = h\nu$. This spectrum line is the first member of an absorption series in the spectrum of the metal. (2) When the velocity of the colliding electron is greater than the ionization potential V_1 the molecule is ionized and the energy lost by the electron is expended in removing an electron from the molecule. In accordance with the Bohr theory of spectra the frequency ν corresponding to the quantum equation $V_1 e = h\nu$ is the limiting frequency of the absorption series. In some cases we have found two resonance potentials and, as will be shown in a subsequent publication, this is a characteristic property of metals of Group II in the periodic table.

Data at present available on electron currents in nonmetallic gases and vapors indicate that the phenomena here observed are more complicated. It is believed that in these elements collisions at all velocities are somewhat inelastic and that there is a tendency for electrons to stick to molecules and form negative ions of large mass.

Spectroscopic data available for these elements give no suggestion of the probable value of critical potentials. No observations of spectra of glow discharge below the ionization potential have been made. Some of the vapors show very complicated absorption spectra in which bands, lines, and regions of continuous absorption occur, while the gases nitrogen and hydrogen in the normal state give no certain evidence of absorption in the regions which it is possible to study. No line series have been found in any of the vapors.

Some of the difficulties in measuring the critical potentials can be foreseen. In metallic vapors which give elastic collisions with low-speed electrons we can determine the lowest potential of inelastic impact with accuracy by increasing the vapor density until the mean free path of electrons is so small that electron velocities can never much exceed the first resonance potential.² However, when low-speed collisions are slightly inelastic, current measurements must be made in a limited range of vapor density. Critical points will not be so sharp, and successive inflections in current-voltage curves due to two resonance potentials may be mistaken for recurrence of collisions of one type only.

The greatest difficulty in studying electron currents in the vapors, however, was the formation of nonconducting films on the electrodes resulting in polarization effects. This could be only partially remedied.

²Franck and Hertz, *Phys. Zeit.*, 17, p. 409, 1916.

II. METHODS OF MEASUREMENT

The type of ionization chamber used in the study of metallic vapors was modified by the addition of a fourth electrode for the more sensitive detection of potentials of inelastic impact. Fig. 1 shows diagrammatically the arrangement of the electrodes. Surrounding the hot wire cathode *A* and as close to it as was conveniently possible was a grid *B*, and a second grid *C* was placed close to the outer electrode *D*. Of the many ways these four electrodes can be connected for the measurement of the various phenomena of electron currents in gases, three at least deserve attention.

Method 1, Fig. 1.—A variable accelerating potential V_1 is applied between *A* and *B*. *B* and *C* are kept at the same potential and a retarding field is fixed between *C* and *D*. Thus through a considerable range of gas pressure electrons will be given their full velocity in the space *AB* before colliding with molecules in the larger part of their path *BC*. As there is no radial electric force in the space *BC* electrons will be kept from reaching the plate by elastic collisions changing their direction, as well as by inelastic collisions changing their speed, and high gas pressure will greatly decrease the plate current. If V_2 is fixed at a comparatively small value, the change in the partial current reaching the plate as the accelerating potential V_1 is varied gives remarkably sensitive indications of potentials of inelastic impact.

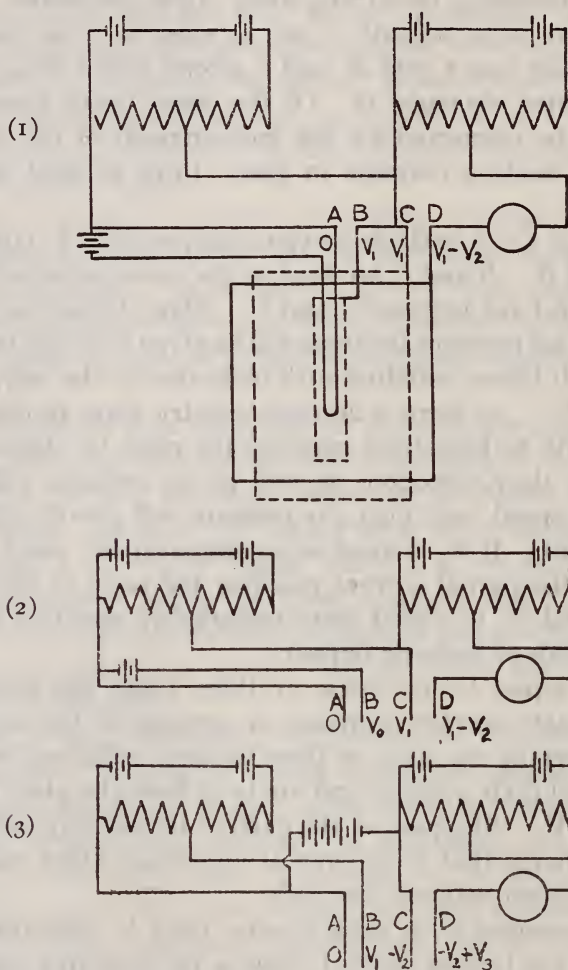
At voltages equal to, or twice, or three times the resonance potential the plate current decreases on account of the fact that electrons undergoing one, two, or three inelastic collisions between the grids lose all their velocity and are kept from the plate by the retarding field V_2 . Stopping of the current is probably enhanced by the space charge that must exist at potentials where electrons are entirely stopped between the grids.

When the potential V_2 is made greater than V_1 ionization can be detected by the Lenard method; that is, by observing the point at which current due to positive charges flows to the plate when V_1 is increased.

While method 1 offers a sensitive method of measuring points of inelastic impact, it is also sensitive to disturbing effects of polarized surface films and it can be used only with limited range of vapor density.

Method 2, Fig. 2.—The inner grid *B* is kept at a fixed relatively small potential V_0 with respect to the cathode while the poten-

tial V_1 of the outer grid is changed. A retarding field as before is placed between the outer grid and plate. Plate currents when V_2 is small show the points of inelastic impact but not as sharply as in method 1 at low gas pressure. Disturbing effects are much diminished. Ionization can be detected as in method 1 by making



FIGS. 1, 2, and 3.—Electrical connections for methods 1, 2, and 3, respectively.

V_2 greater than V_1 . It can also be observed by measuring the total electron current reaching the outer grid and plate since this will increase at the ionization point. It may be noted that while the current leaving the cathode is nearly constant as V_1 is changed, the part of the current getting through the inner grid increases as V_1 is increased.

Davis and Goucher³ have shown that with an ionization chamber connected by the Lenard method, viz, V_2 greater than V_1 in either method 1 or 2, radiation emitted in the glow discharge at the resonance potential may give a photoelectric current between the plate and outer grid indistinguishable in these methods of measurement from the current due to ionization. The following method of distinguishing ionization and radiation is practically identical with the method used by them.

Method 3, Fig. 3.—The variable accelerating potential V_1 is applied between the cathode and the inner grid. The outer grid is kept at a potential $-V_2$ and the plate at $-V_2 + V_3$. Thus no electrons from the cathode can reach the plate. Ions formed near the inner grid will reach the plate after falling through the potential $-(V_1 + V_2)$, in spite of the relatively small retarding field V_3 ; but photo-electrons emitted from the grid and plate with a small velocity will give a current in the direction of V_3 and opposite to the ion current.

Measurements with method 3 have not in our hands given nearly as accurate results as can be obtained from measurement of the partial current reaching the plate against a small retarding field, but the method was useful in distinguishing ionization and radiation effects in hydrogen. Measurements by the Lenard method with connections of method 1 gave much sharper inflections at the critical potentials for both radiation and ionization.

III. MEASUREMENTS IN THE VAPORS OF PHOSPHORUS, IODINE, AND SULPHUR

Disturbing effects of surface films on electrodes presented the chief difficulty in this work. Frequent renewal of the electrodes and suitable choice of materials reduced the trouble but did not eliminate it. Resonance potentials were measured from successive inflections in the plate current curves obtained by method 1 or 2. Ionization potentials were measured by the Lenard method with the same galvanometer sensitivity as used for the resonance curves and were corrected from the observed initial potential of the resonance curve. As the observed ionization point depends somewhat on the galvanometer sensitivity, it is necessary to keep this the same for the two curves.

The form of vacuum tube used was a large pyrex tube 8 by 30 cm, closed at the bottom and with a metal plate supporting the

³ Phys. Rev., 10, p. 101, 1917.

electrodes sealed in the top. Electrodes of sheet steel and iron gauze were used with phosphorus, while nickel and an inner grid of platinum were used in iodine. With sulphur a plate of aluminum and grids of platinum gave best results. The plate in each case was a cylinder fitting the pyrex tube, and the other electrodes were in the proportions shown in Fig. 1. The cathode used in phosphorus and iodine was usually a bare incandescent molybdenum wire, as oxide coatings were attacked by the vapors and were practically useless for increasing thermionic emission. Platinum strips coated with burned sealing wax were satisfactory in sulphur vapor. The temperature of the tube was controlled by baths of ice or water or by an electric furnace surrounding the lower part of the tube. It was always necessary to keep the electrodes at a higher temperature than the rest of the tube to avoid the condensation of an insulating layer on them. A vacuum of about 0.001 mm was maintained by mercury vapor pumps and a trap cooled in liquid air or carbon-dioxide snow was placed between the pumps and ionization chamber. Currents were measured on a sensitive galvanometer and were of the order of 10^{-8} amperes.

1. PHOSPHORUS

Fig. 4 gives typical curves obtained with phosphorus vapor using the first method of measurement. Curves 19, 22, 28, 31, and 38 are the electron current reaching the plate against a small retarding field. Curves 6, 9, and 32 are of positive current reaching the plate when the retarding field is large, viz, the Lenard method. Table 1 gives the results of all the curves obtained with notes on conditions of observation. From the curves shown it is seen that phosphorus has a definite resonance potential. The ionization point is not very sharp but is unmistakable. Attempts to obtain more inflections in the partial current curves by increasing the vapor density reduced the current to an immeasurable value.

The curves were obtained under a wide range of conditions, as is shown in Table 1. Curves 6, 9, 19, and 22 of Fig. 4 were obtained in the vapor of yellow phosphorus at about room temperature. Under these conditions the vapor condenses in the form of a red film, evidently a mixture of red and yellow phosphorus. Curves 28 and 38 were obtained in the vapor of red phosphorus at about 400° C. At this temperature the vapor condenses in cold parts of the tube in a red film as before and in the hot part in a gray

crystalline form. After once heating red phosphorus to about 450°C and getting the red film on cold parts of the tube, vapor pressures suited for current measurements were obtained in a wide range of temperature. Curves 31 and 32 were obtained at room temperature after the tube had been heated. The similarity of all the curves in the temperature range 420°C to 15°C indicates that the constitution of the phosphorus molecule in the vapor

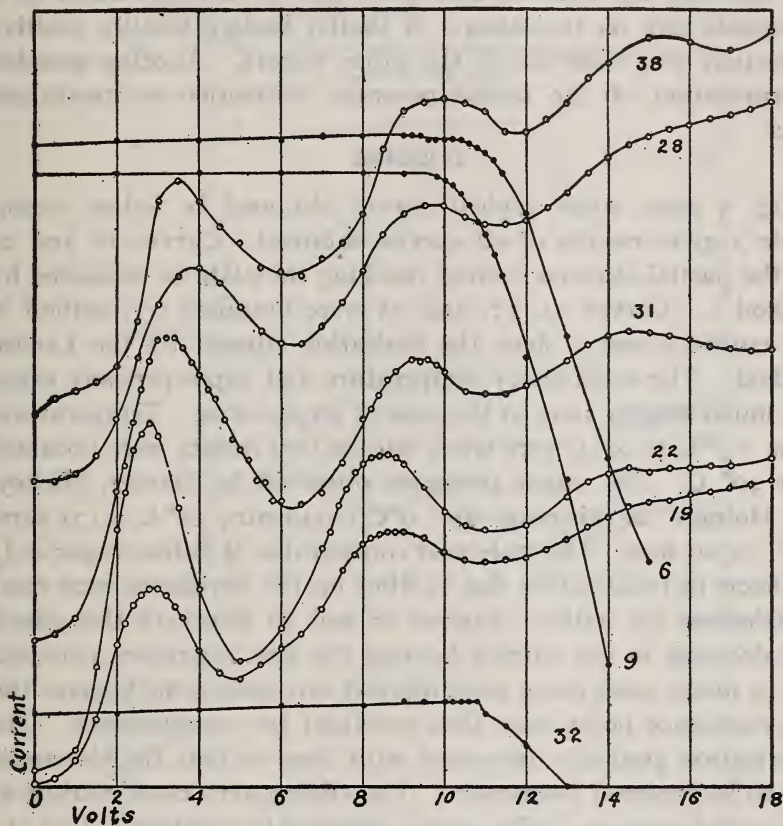


FIG. 4.—Current-voltage curves for phosphorus

state does not change in this range. The molecular constitution of phosphorus vapor at 300°C is given as P_4 .

The mean values from the 43 curves are summarized as follows:

| | Volts |
|---------------------------|----------------|
| Resonance potential..... | 5.80 ± 0.1 |
| Ionization potential..... | $13.3 \pm .5$ |

As can be seen from Table I, the individual measurements of resonance potential do not differ from the mean by more than the

probable observational error, but there is more variation in the ionization potentials, probably arising in the method of applying initial potential corrections. A striking feature of the partial current curves is the large initial potential correction; that is, the difference between the resonance potential and the applied potential at the first resonance point. Clearly it is not a velocity correction in this case but probably a contact difference of potential between the cathode and grids due to the formation of a phosphide film on the latter. A similar though smaller positive correction was observed in the other vapors. Another possible interpretation of the initial potential correction is mentioned later.

2. IODINE

Fig. 5 gives some typical curves obtained in iodine vapor. Table 2 gives results of all curves obtained. Curves 16 and 22 are the partial electron current reaching the plate as measured by method 1. Curves 13, 17, and 25 were obtained by method 2, and curves 4 and 6 show the ionization current by the Lenard method. The satisfactory temperature and vapor-pressure range was much smaller than in the case of phosphorus. Temperatures from -5°C to 30°C were tried, but the best results were obtained near 20°C . The vapor pressures observed by Baxter, Hickey, and Holmes⁴ in this range are: 0°C , 0.030 mm; 15°C , 0.131 mm; 25°C , 0.305 mm. The molecular constitution of iodine vapor is I_2 .

Effects of polarization due to films on the electrodes were most troublesome for iodine. Curves 16 and 22 illustrate this effect. The decrease in the current beyond the first resonance potential was in many cases much more marked but inflections beyond the first resonance point were then too faint for measurement. The polarization gradually increased with time so that the electrodes had to be renewed frequently. The effects were most marked at high vapor pressure. The curves obtained by method 2 show the effect much less than method 1.

The fact that the curves obtained under various conditions give values of the resonance potential not varying from the mean by more than the probable uncertainty of picking out the points of inflection on the curves is good evidence that this method of measuring the resonance potential is reliable until disturbing effects entirely mask the inflections due to inelastic impact. Measurements of ionization potential as in the case of phosphorus

⁴ Jour. Amer. Chem. Soc., 29, p. 127; 1907.

show a larger observational error though the percentage error is probably less. The mean values are as follows:

| | |
|---------------------------|----------------|
| | Volts |
| Resonance potential..... | 2.34 ± 0.2 |
| Ionization potential..... | $10.1 \pm .5$ |

This is the first measurement that has been made of the resonance potential. The ionization potential has been measured

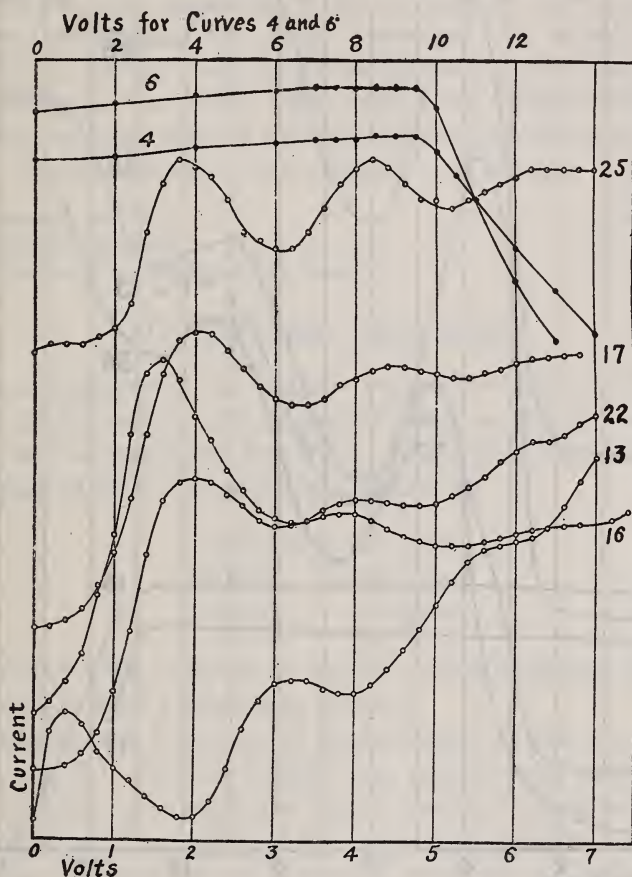


FIG. 5.—Current-voltage curves for iodine

by C. G. Found⁵ from the current voltage curve obtained in a two-electrode tube as 8.5 volts. The presence of a contact potential difference of about 1 volt, observed by us but of course impossible to detect in a two-electrode tube, would explain the difference between our results.

⁵ Phys. Rev., 15, p. 132; 1920.

3. SULPHUR

Table 3 gives the results obtained in sulphur vapor, and Fig. 6 shows some typical curves. Curves 3, 22, and 26 show the partial electron current reaching the plate as measured by method 1. Curve 30 shows the same obtained by method 2. Curves 11 and

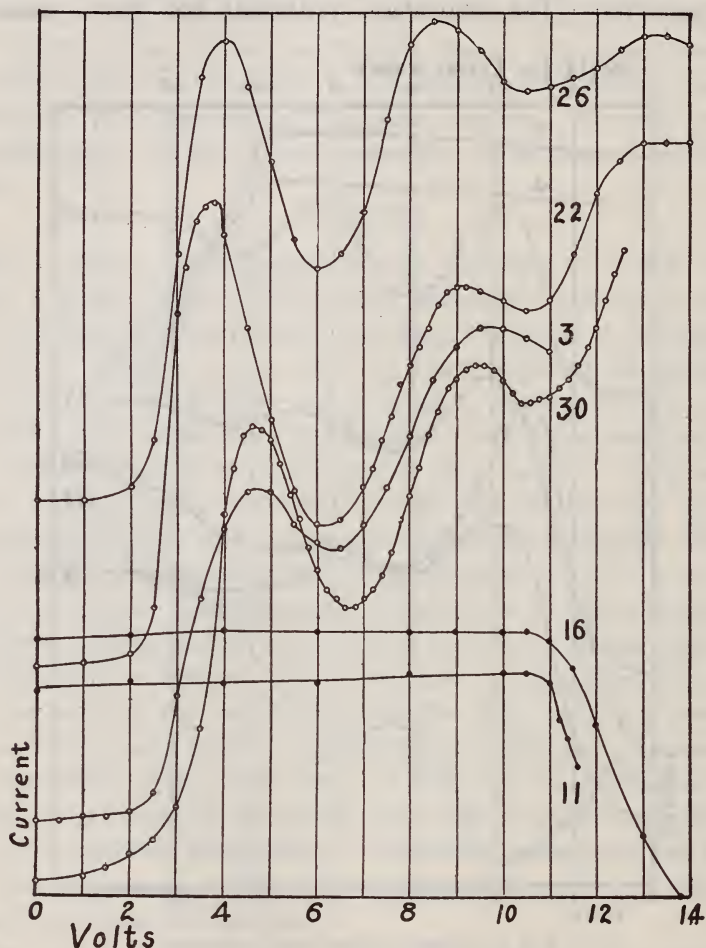


FIG. 6.—Current-voltage curves for sulphur

16 show the ionization point by the Lenard method. Measurements were made in the temperature range 120°C to 170°C . The probable molecular structure of the vapor is S_8 .

Difficulty with unsteady currents was a source of trouble in these measurements but this unsteadiness gradually decreased if the temperature was held constant for some time. The cause

of this was unknown. As can be seen from Fig. 6 the curves show inflections capable of fairly accurate measurement, but, unlike the other vapors, the agreement between results from different curves is scarcely within the probable error in picking out the points. It can be seen from the figure that in some of the curves the second resonance inflection is not halfway between the first and third. The existence of two resonance potentials is a probable explanation. Determination of the ionization potential gave as consistent results as the other elements. An unpublished research by Foote and Rognley on the ionization potential in which initial potential corrections were made from velocity distribution curves also gave a result in close agreement with the results of this work. The final summary for sulphur is as follows:

| | Volts |
|-----------------------------------------------|----------------|
| Resonance potential..... | 4.78 ± 0.5 |
| Ionization potential..... | $12.2 \pm .5$ |
| Ionization potential (Foote and Rognley)..... | 12.1 |

IV. SPECTRAL RELATIONS

From analogy with the metallic vapors the resonance potential should correspond by the quantum relation $Ve = h\nu$ to the frequency of the single-line spectrum. The following wave lengths are computed from the resonance potentials:

| | |
|------------|------------------------------|
| Phosphorus | $\lambda = 2130 \text{ \AA}$ |
| Iodine | $\lambda = 5300 \text{ \AA}$ |
| Sulphur | $\lambda = 2580 \text{ \AA}$ |

It has not been possible to identify these predicted lines from spectroscopic data available at present.

The absorption spectrum of phosphorus has not been studied beyond 2200\AA .⁶ In both iodine⁷ and sulphur⁸ the predicted line lies in a region of complicated band spectra and, at least in the case of iodine, in a region of line-absorption spectra as well, but with lines closer than the probable error of our measurement. Probably in the case of phosphorus also the predicted line lies within a wide region of band spectra, as bands are observed to the limit of the region photographed.

⁶ Kayser and Runge, Handbuch.

⁷ R. W. Wood, *Astrophys. Jour.*, 46, p. 181; 1917.

⁸ Dobbie and Fox, *Proc. Roy. Soc., London*, 95, p. 484; 1919.

V. MEASUREMENTS IN THE COMMON GASES

1. INTRODUCTION

A four-electrode vacuum tube of the same general form as described in Section II was used to study electron currents in nitrogen, oxygen, and hydrogen. The ionization chamber was made of platinum electrodes sealed in a glass tube about 3 cm in diameter. The grids were of fine platinum gauze supported on heavier strips, and the plate was a cylinder of platinum foil fitting tightly in the tube. A hot platinum strip coated with burned sealing wax served as a cathode. Connecting tubes to the pump and the gas reservoir were arranged so that gas could be streamed through the tube or kept stagnant while liquid-air traps on each side of the ionization chamber froze out any condensable impurities.

In the study of electron currents in these gases we are able to consider another effect of collision besides loss of electron velocity and ionization, namely, the effect of radiation, emitted above the resonance potential, on the outer electrodes, causing photo-electric emission from them. As the long wave-length limit of platinum is about $\lambda=2800 \text{ \AA}$, this effect must be present whenever the resonance potential is above 4.5 volts, but with our apparatus it has been too small to measure in all the elements previously studied. The radiation effect has further interest in research on the gases, since in most of the considerable amount of work of other observers the resonance potentials have been observed by means of the radiation effects.

The Lenard method as used in Section II for the measurement of ionization potentials will show this radiation effect at the resonance potential as a current in the same direction as the ionization current. Davis and Goucher⁹ devised a method described under method 3 for distinguishing effects of radiation and ionization. When precautions are taken to distinguish the two effects, we have a valuable means of measuring critical potentials, which is entirely distinct from the method of inelastic collisions here used. However, in all the work previous to the research of Davis and Goucher the simple Lenard method was applied with the assumption that the presence of a plate current was conclusive evidence of ionization. The uncertainty as to just what was measured accordingly vitiates nearly all this early work.

⁹Phys. Rev., 10, p. 84; 1917.

2. NITROGEN

Various observers using the Lenard method have given values of about 7.5 volts for the ionization potential of nitrogen. Davis and Goucher¹⁰ have by their method found radiation alone at 7.4 volts, further radiation at 9 volts, and ionization at 18 volts, H. D. Smyth¹¹ has used the radiation method in a three-electrode tube, making careful corrections for initial potential, with the following results: Radiation, 8.29 volts; a secondary radiation effect at 6.29 volts; and ionization, 18 volts. Found,¹² using a two-electrode tube, observed ionization at about 16 volts. Akesson¹³ has applied the method of observing the potentials of inelastic collisions, but under quite different conditions from those we have used, and obtained the value of 1.7 volts.

In our work commercial nitrogen was passed through hot copper, calcium chloride, and liquid-air traps. Pressures ranging from 0.1 mm to 2 mm were used. Streaming gas was used where possible, but at the higher pressures currents were steadier in stagnant gas. The Davis and Goucher method was applied with results agreeing roughly with theirs, but the curves obtained were not sharp enough to furnish accurate values of the critical potentials. Measurements with connections of method 1 proved capable of much higher accuracy. Measurement of the total current with method 2 gave a valuable check on the other ionization potential measurements. Table 4 gives a summary of all the curves obtained which were capable of accurate analysis.

An upper limit to the gas pressure that can be used is set by the striking of an arc between the cathode and inner net, but arcing between the nets at lower pressure has also been found troublesome when the current density is large. The arcing potential is above the ionization potential, and the amount above and the sharpness increase with the pressure. It is indicated by a break in the current voltage curves very sharp in contrast with the critical points. Evidently when the proportion of positive ions formed by collision reaches a definite value the negative space charge surrounding the cathode is suddenly replaced by a positive space charge. The resulting increase in the electric force at the surface of the cathode causes a sudden increase in the thermionic emission. It is possible that the high values obtained for the ionization potential by Davis and Goucher and by Smyth are due

¹⁰ Phys. Rev., 13, p. 1; 1919.

¹² Phys. Rev., 15, p. 132; 1920.

¹¹ Phys. Rev., 14, p. 409; 1919.

¹³ Lunds Universitets Arsskrift N. F. Avd., 2 Bd.: 2 Nr., 111.

to mistaking the arc point for the true ionization point. A characteristic feature of this arc point is that the break in the curve as the potential is increased is above the break when the potential is decreased. This result is in accord with the explanation given above.¹⁴

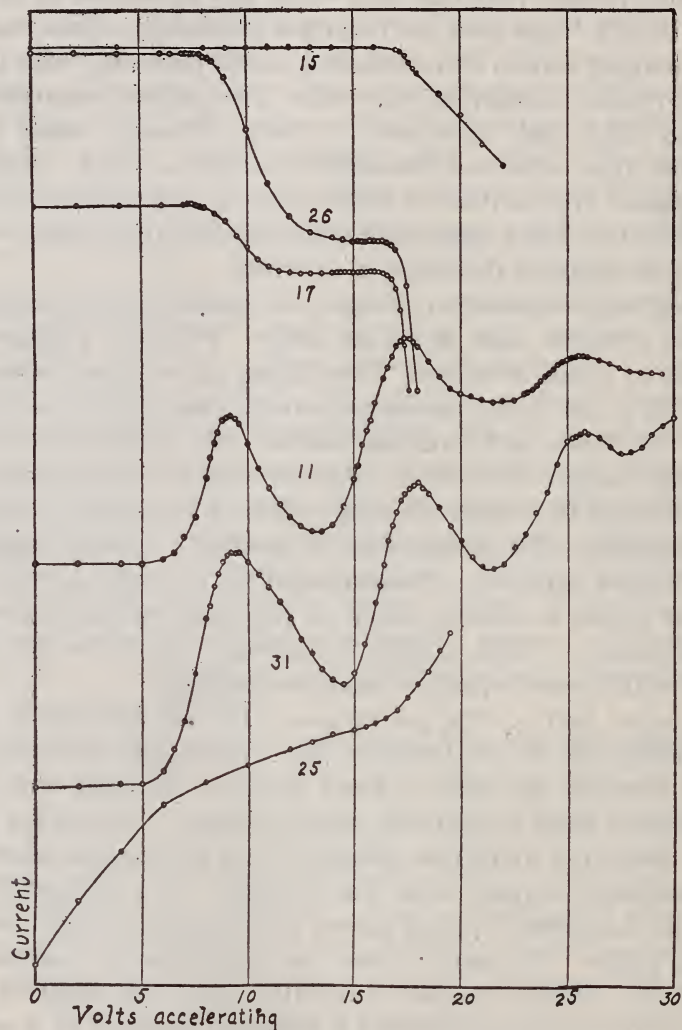


FIG. 7.—Current-voltage curves for nitrogen

Fig. 7 shows some typical curves. Curves 11 and 31 are plate current *vs.* potential, using connections of method 1 with V_2 small. They show inflections due to successive resonance collisions of only one resonance potential. A slightly higher second resonance

¹⁴ Foote, Rognley and Mohler, loc. cit. Horton and Davies, Proc. Roy. Soc., 37, p. 1; 1920.

potential might have been missed, but the existence of a lower secondary resonance potential as observed by Smyth should be best detected by this method. The existence of inelastic collision at 1.7 volts as observed by Akesson was not verified.

Curves obtained with V_2 greater than V_1 and relatively high galvanometer sensitivity are illustrated by curves 17 and 26. They show sharply both the occurrence of the radiation effect starting at the resonance potential and of ionization. The best results were secured with rather low gas pressure. From these curves the potential difference between the resonance and ionization points may be accurately measured.

If this Lenard method is applied with the much smaller galvanometer sensitivity and higher gas pressure used in observing the resonance potential curves a measurable current is not obtained until the ionization potential is reached, and the potential between the two points can be determined as before in Part I. Curve 15 illustrates this method.

A third method applicable to nitrogen is to observe the point where the total current from the cathode increases and correct for initial potential as before (curve 25).

The various methods agree well, giving as a mean result the following values:

| | |
|---------------------------|---------------------|
| Resonance potential..... | Volts 8.18 ± 0.1 |
| Ionization potential..... | 16.9 ± .5 |

As shown by Smyth the resonance potential corresponds by the quantum relation $Ve = h\nu$ or $V = \frac{12345}{\lambda}$ to the isolated doublet in the nitrogen spectrum observed by Lyman¹⁵ at $\lambda = 1492.8 \text{ \AA}$ and 1494.8 \AA . The wave length $\lambda = 1492.8$ gives $V = 8.27$ volts as the theoretical value. The ionization potential predicts for the limiting wave length $\lambda = 730 \text{ \AA}$.

3. OXYGEN

Values of about nine volts have been given for the ionization potential of oxygen by a number of observers. The conclusions were drawn from application of the Lenard method, and the radiation effect is undoubtedly what was observed. Akesson¹⁶ observed inelastic impact at seven volts.

In our experiments with oxygen the gas was generated electrolytically and dried as before. Pressures ranging from 1 mm to 0.2 mm were used.

¹⁵ Lyman, The spectroscopy of the extreme ultraviolet, p. 113.

¹⁶ Loc. cit.

The phenomena of electron currents in oxygen are quite different from nitrogen though the critical potentials are in the same region. The radiation effect is very small and the point at which it starts difficult to determine, though the points of inelastic collision are nearly as sharp as in nitrogen. Arcing above the ionization potential was not observed in the entire range of pressures that could be used, and no visible glow was observed in the vacuum tube. However, the ionization potential was very distinct in contrast to the radiation effect and of a magnitude comparable to the electron

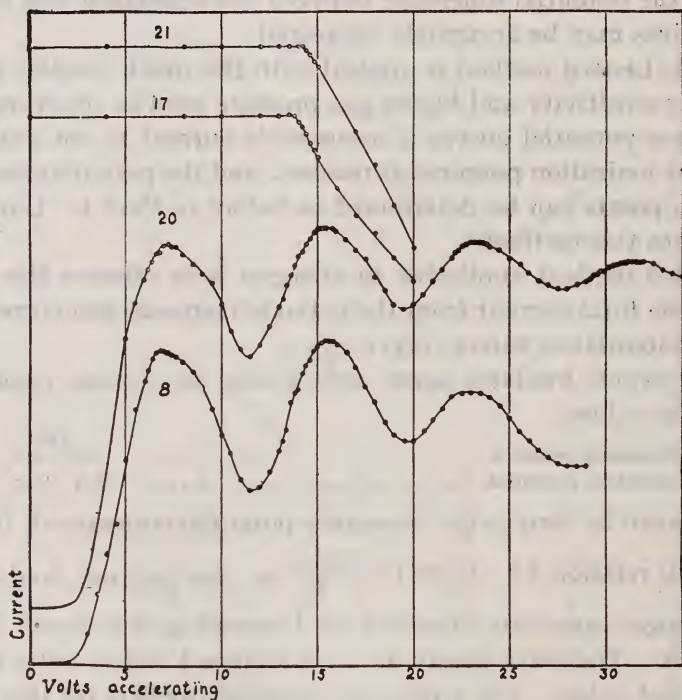


FIG. 8.—Current-voltage curves for oxygen

current. The measurements of critical potentials were therefore made as with the vapors, viz, by obtaining two consecutive plate-current voltage curves by method 1, one with V_2 small, showing points of inelastic impact, and one with V_2 large, showing ionization, and by measuring from the two the resonance potential and the difference between the ionization and resonance potentials.

Table 5 gives a summary of the conditions of measurement and analysis of all the curves. Fig. 8 gives typical curves. The accuracy attained with oxygen is probably slightly higher than with nitrogen on account of the absence of arcing effects.

The final values are as follows:

| | Volts |
|----------------------------|----------------|
| Resonance potential | 7.91 ± 0.1 |
| Ionization potential | $15.5 \pm .5$ |

The resonance potential gives by the quantum relation $\lambda = 1560$ Å for the single-line spectrum and $\lambda = 796$ Å for the limiting frequency. The wave length $\lambda = 1560$ falls within the great oxygen band at $\lambda = 1800$ to 1300 Å. No line spectra have been observed with certainty in this region.

4. HYDROGEN

The value of the critical potentials in hydrogen is of peculiar interest since the development of the Bohr¹⁷ theory. However, the fundamental theory predicts the potentials for only the hydrogen atom. An extension of the theory has been made by Bohr and by Debeye to the case of the normal H_2 molecule, but this extension involves assumptions not included in the fundamental theory, and it may be open to even greater doubt.

To ionize the hydrogen atom in the normal condition, i. e., with its single electron in the innermost stable orbit, requires an amount of work proportional to the Rydberg number, or a potential of 13.54 volts.

The work required to remove the electron from the innermost orbit to the next stable orbit is proportional to three-fourths of the Rydberg number, giving a resonance potential of 10.16 volts. The Rydberg number and three-fourths of this number are, respectively, the limit and first line of the Lyman series. As to the hydrogen molecule, the Bohr model in which the two electrons revolve in coplanar orbits around the line joining the two nuclei as an axis requires for ionization an amount of work equal to the ionization potential of the atom plus the work of dissociation of the molecule. His theory gives this ionization potential as 16.26 volts, making the work of dissociation 2.72 volts. Langmuir's experimental determination of the heat of dissociation of hydrogen as 90 000 calories per gram-molecule gives the work of dissociation as 3.9 volts. Bohr's theory of molecular hydrogen does not predict the value of a resonance potential for the molecule.

Experimental determinations of the critical potentials of hydrogen have in the past seemed irreconcilable with this theory. Lenard, Mayer, Bishop, and others found ionization at 11 volts using the simple Lenard method. Davis and Goucher¹⁸ by their

¹⁷ Phil. Mag., 26, pp. 1, 476, 857; 1913.

¹⁸ Phys. Rev., 18, p. 84; 1917.

method found, besides ionization at 11 volts, a second ionization at 15.8 volts and radiation at 13.6 volts. More recently Frank Knipping and Kruger¹⁹ have by a similar method found ionization at 11.5 volts, 17.1 volts, and 30.4 volts, and radiation at 13.6 volts

Since our work described below was completed, a paper by Horton and Davies²⁰ has appeared in which they have arrived at conclusions similar to those obtained independently by us and much more in accord with theory. They find radiation alone at 10.5 volts, further radiation at 13.9 volts, ionization at 14.4 volts and 16.9 volts.

The problem of distinguishing and measuring these four potentials which occur in the interval 10 to 17 volts is considerably more difficult than the measurements in other gases showing only two critical points.

In our work electrolytic hydrogen was dried as before, and either streamed through liquid-air traps or kept stagnant while readings were taken. The ionization chamber was used in the same form as before and also with cathodes of palladium strips and bare tungsten wire. Also a much larger ionization chamber with nickel electrodes similar to the one used with the vapors was tried. Results obtained under these varied conditions were not notably different.

In preliminary experiments method 3, the Davis and Goucher method was used to distinguish radiation and ionization effects, but with results quite contrary to theirs. At about 10 volts a radiation effect alone was observed, and there was a strong ionization effect at 16 volts. By decreasing the gas pressure and consequently the radiation effect the ionization effect could be detected at a lower point around 13 volts. The curves obtained by this method were not sharp enough to give accurate values for the critical potentials. The methods used with the other gases, namely, measurement of inelastic impacts by method 1 and of ionization by the Lenard method with connections of method 1 were applied as before for the measurement of the potentials.

Fig. 9 shows the types of curves obtained. Curves 37, 64, 65, and 18 show points of inelastic impact, while 54, 30, and 31 show curves obtained by the Lenard method. The curves show many variations as pressure and current density are changed. Thus curves 18 and 65 show two successive resonance collisions near 10

¹⁹ Ber. Deut. Phys. Ges., 21, p. 728: 1919.

²⁰ Proc. Roy. Soc.: March, 1920.

and 20 volts and between these points a sharp break due to the second ionization potential. Curve 64 shows inflections due to the first resonance potential alone, while 65 shows a definitely greater interval between inflections which probably measures a second resonance potential. Curves of this latter type could be obtained only under a small range of conditions. Unfortunately

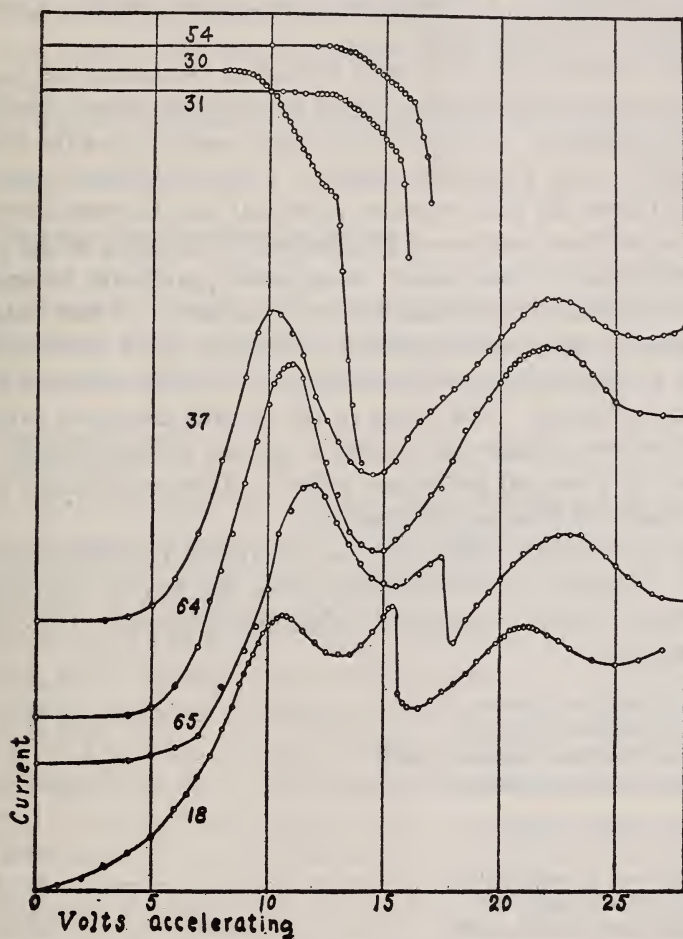


FIG. 9.—Current-voltage curves for hydrogen

our apparatus and method did not serve to separate the two resonance potentials so as to measure both from the same curve. Many of the curves showed a broadening out of the inflection near 20 volts that may be well explained by the superposed effect of two resonance potentials. Curves 64 and 65 show this effect to a slight extent.

Curve 30 was taken with the Lenard method using high galvanometer sensitivity and shows the radiation effect starting at 9 volts and the first ionization point at 12.5 volts. Only a few curves could be obtained showing both these points sharply.

Curve 31 was taken under the same conditions except that the galvanometer sensitivity was much less, so that the radiation effect was immeasurable. It shows both ionization points. Curve 54 is another of the same type.

Curves of the type of 65 and 18 suffice to determine the first resonance potential and the interval between the second ionization and first resonance. Curves of the type 54 and 31 give the interval between the two ionization points. Curves of these two types combined give the first resonance potential and the two ionization potentials without any use of the method of applying initial potential corrections of one curve to applied potentials in another. Our final results were obtained in this manner. A few values of the interval, first resonance-first ionization, from curves of the type of 30 check the value obtained by the other method within experimental error. The value of the second resonance potential is based on fewer observations and is subject to some doubt. The existence of a second resonance point is, however, clearly shown in the results of Horton and Davies.

Table 6 gives the measurements of critical potentials from 71 curves. The note at the bottom gives the key to the identity of the five different points of inflection observed. Our results are as follows:

| | Volts |
|----------------------------------------|-----------------|
| First resonance potential..... | 10.40 \pm 0.5 |
| First ionization potential..... | 13.3 \pm .5 |
| Second resonance potential, about..... | 12.2 |
| Second ionization potential..... | 16.51 \pm .5 |

Bohr's theory gives:

| | Volts |
|-------------------------------------|-------|
| Resonance potential of H_1 | 10.16 |
| Ionization potential of H_1 | 13.54 |
| Ionization potential of H_2 | 16.26 |

The conclusion that we have observed the resonance potentials and ionization potentials of both H_1 and H_2 is fairly evident. The question arises as to whether or not hydrogen is dissociated without being ionized by electron impact. The energy required is equal to that of an electron falling through 2.7 volts on Bohr's theory or 3.9 volts from Langmuir's value of the heat of dissociation. No certain evidence of inelastic impact in this low range

of voltage was found, though the possible existence of a non-selective stopping of low voltage electrons is apparent in some of the curves. Certainly, however, there is dissociation of hydrogen by the catalytic action of the hot cathode²¹ (platinum, palladium, or tungsten).

A consequence of the Bohr model for the hydrogen molecule is that the difference between the ionization potentials of the molecule and atom is the work required to dissociate hydrogen into its atoms.

Our observed difference between ionization potentials gives:

| | Volts |
|-------------------------------------------------|----------|
| Work of dissociation..... | 3.24±0.5 |
| Bohr's theory..... | 2.72 |
| Langmuir's value from heat of dissociation..... | 3.9 |

A better check on the theory is obtained from the interval first resonance potential to second ionization potential, as this interval is the most accurate one given by our observations, being based on measurements of 34 curves showing both points sharply.

| | Volts |
|-------------------------|----------|
| Experimental value..... | 6.11±0.2 |
| Bohr's theory..... | 6.10 |

The values obtained by other observers for these intervals give results that are likewise close to the values predicted by Bohr. Thus Horton and Davies get 2.5 volts difference between ionization points and 6.4 volts between first resonance and second ionization. Frank Knipping and Kruger observe ionization at the first critical potential, but, assuming that the ionization is a secondary effect occurring at the first resonance potential, their results give an interval of 5.6 volts, which is, within their experimental error, in agreement with the 6.1 volts predicted by theory. The interval observed by Davis and Goucher of 4.8 volts is not very close, but there is evidence that their method of correcting for initial potential is subject to error. As the Bohr-Debye model of the hydrogen molecule is far from being an accepted theory, this close agreement between the experimental and predicted value for the ionization potential is an unexpected result. Certainly the interval between ionization potentials is less than the work of dissociation as derived from Langmuir's results, viz, 3.9 volts. Frank Knipping and Kruger identify this work with the interval between their observed resonance point at 13.6 and ionization at 17.1, but there is no theoretical basis that we can see for this deduction.

²¹ Langmuir, J. Am. Chem. Soc., 34, p. 860: 1912.

Bohr has not predicted the interval between resonance potentials, but experimental evidence shows that it is about the same as the interval between ionization potentials. If this were true, the second resonance potential should be at 12.9 volts. Possibly the assumption that the ratio of resonance potentials equals the ratio of ionization potentials is more in accord with theory. This would give 12.2 volts for the second resonance, with an interval between resonance potentials of 2 volts. The experimental data on this interval are inaccurate but range around the two values 12.9 and 12.2. Thus Horton and Davies observe the interval between resonance potentials as 3.4 volts; Davis and Goucher, 2.5 volts; Frank Knipping and Kruger, 2.1 volts; and our result is 1.8 volts.

The interval, second resonance-second ionization, would on this interpretation be 4.1 or 3.4 volts. The interval as observed by Frank et al. is 3.5 volts; by Horton and Davies, 3; by us, 4.3.

This rather detailed consideration shows that the results of various observers when properly interpreted are not discordant beyond experimental error except on one point, viz, the nature of the first critical potential. Assuming that this is in each case the first resonance potential and that the ionization observed by some is a secondary effect, the results of all observers agree within the probable experimental error with the Bohr theory of what would be observed in a mixture of H_1 and H_2 . The experimental differences may seem large, but the overlapping of effects due to the second resonance and first ionization is a serious difficulty in the radiation methods of measurement. The value of the interval first resonance to second ionization is the best check of the theory with our method of measurement.

VI. CONCLUSION

Table 7 gives a summary of the critical potentials of the six elements studied in this paper together with the related spectral lines and limiting wave lengths. The wave lengths in italics are computed from observed potentials.

Excepting the case of hydrogen these elements all show a resonance and ionization potential similar in relative magnitude to those observed in metallic vapors. Except for the cases of iodine and sulphur the actual magnitudes of the potentials are larger than the potentials observed in any of the metals. In the case of sulphur there is evidence that there are two resonance potentials and

but one ionization potential, which is again analogous to some of the metals.²² The most marked difference between electron currents in these elements in comparison with metallic vapors is a lack of sharpness in the critical potentials, which becomes more marked as the pressure is increased. It is undoubtedly due largely to the fact that electron collisions are slightly inelastic at all potentials. No quantitative measure of this was obtained from our experiments. The effect was largest in iodine and decreasingly less in sulphur, oxygen, phosphorus, nitrogen, and hydrogen. The order given is doubtful but is seen to agree roughly with the order of electronegative properties of the elements.

Another property generally ascribed to nonmetallic elements is the tendency to form, in the vaporized state, negative ions; that is, they possess an affinity for electrons.²³ The existence of the negative ions may be shown by measurements of mobility. Accordingly, it appears that a neutral atom of iodine for example, exerts an attractive force upon an electron of such a magnitude that an amount of work must be done on the negative ion, to separate it into a neutral atom and an electron, equivalent to that developed by an electron in falling through E volts. Born has suggested the term "negative ionization potential" for E .²⁴

From a consideration of the "grating energy" of halogen salts, the heat of formation of the salt from its elements, the heat of sublimation of the metal, the heat of dissociation of the halogen, and the ionization potential of the neutral metal atom it is possible to compute the value of E for the halogen gases. In the case of iodine this amounts to -3.3 volts. Hence it would appear that an electron having a velocity of less than 3.3 volts sticks to an iodine atom, upon collision, forming a negative ion. The heat of dissociation of I_2 into $2I$ is 1.6 volts, so that the electron affinity of either atom in the molecule is greater than the force holding the two atoms together. Hence a neutral molecule, as suggested by Fajans, might spontaneously or with slight excitation, at least as far as the energy relations are concerned, dissociate producing one neutral atom, a negative atom, and $(3.3-1.6) e$ of energy, possibly emitted as radiation.

The ionization curves for iodine did not, as in the case of hydrogen, show the presence of two ionization potentials differing in magnitude by the heat of dissociation. However, since iodine

²² This latter point will be discussed in a forthcoming paper on metals of Group II of the periodic table.

²³ Franck, *Verh. d. Phys. Ges.*, **12**, pp. 291, 613, 1910; *Jahrb. d. Radioakt. u. Elek.*, **9**, p. 259: 1912.

²⁴ See series of papers by Born, Fajans, and Haber in *Ber. d. Phys. Ges.*, 1919.

is readily dissociated by the hot wire at the temperatures employed, some monatomic vapor must be present, especially so on the basis of the above highly speculative theory. The number of electrons leaving the hot wire in a few seconds is comparable to the total number of atoms of iodine present, so that if this electron affinity existed a large portion of the iodine might readily consist of negatively charged atoms. This condition is analogous to that obtained with a metallic vapor above the ionization potential. In this latter case the number of electrons leaving the cathode with velocity sufficient to ionize, greatly exceeds any measureable ionic current, even when the mean free path of an electron is such that every electron produces ionization, because of recombination, as evidenced by the increased production of radiation. Hence it may be possible that the observed resonance potential of iodine and other nonmetallic vapors refers to the negatively charged atom rather than to the neutral atom or molecule. In the case of ionization positive iodine atoms or molecules are found, as shown by the downward bend in the curves illustrated. Hence, if negative atoms are present in preponderance, the ionization potential must be the work necessary to eject at least two electrons from the iodine ion.

The existence of the observed high initial potentials on the above hypothesis may be due to the formation of a layer of neutral iodine atoms on the inner net, attracted to the net by their electron affinity.

Were it not for the well-established experimental facts in regard to the electron affinity of these nonmetallic vapors we would be likely to conclude from our work that the behavior of these vapors is quite similar to that of metallic vapors and accordingly might question the existence of a "negative ionization potential." Certainly the general type of curves obtained with nonmetallic vapors is not materially different from that for the metallic vapors, but as stated above this might still be the case even though we are concerned with negative ions instead of neutral atoms.

The question as to whether the critical potentials are atomic or molecular properties is an important point. Hydrogen with its two resonance and ionization potentials is apparently unique. The curves are best explained as due to a mixture at least near the cathode of H_2 and H_1 in proportions varying with experimental conditions. Nitrogen is certainly much less dissociated than hydrogen under similar conditions so it would seem that the

single resonance and ionization potentials observed for it must be ascribed to N_2 molecules. However, the resonance potential corresponds to a frequency of the line emission spectrum and not of the band spectra. We must then admit that line spectra can be emitted by molecules, which is contrary to the generally accepted view that polyatomic molecules give rise to band spectra only.

Oxygen is probably similar to nitrogen in this respect. The ionization point for the vapors may refer to the condition of the vapor which exists predominantly in the tube, i. e., molecules, neutral atoms, or negatively charged atoms, or if all conditions are present, it is most likely the lowest ionization potential for the three states, accordingly for the neutral atom, if the theory of negative ionization potential is true.

Definite conclusions require further experimental work in other directions. The study of the vapors from the spectroscopic standpoint, similar to the work carried out with *cæsium*,²⁵ offers the most promising field. The single-line spectra are in spectral regions favorable for observation, and the physical conditions for dissociation of the molecules are obtainable in the laboratory.

WASHINGTON, May 29, 1920.

²⁵ Foote and Meggers, B. S. Sci. Papers No. 386.

TABLE 1.—Resonance and Ionization Potentials of Phosphorus

| Curve | Remarks | Temperature | Applied potentials | | | Resonance potential | Initial potential | Ionization potential |
|---------|-----------------------------|-------------|--------------------|-----|---------------|---------------------|-------------------|----------------------|
| | | | At resonance | | At ionization | | | |
| | | | a | b | | b-a | | |
| | | °C | | | | | | |
| 1..... | 3 electrodes..... | 28 | 4.8 | | 12.4 | | 1.0 | 13.4 |
| 2..... | do..... | 28 | 4.6 | | 12.4 | | 1.2 | 13.6 |
| 3..... | 4 electrodes, yellow P..... | 25 | 3.5 | 9.5 | | 6.0 | 2.3 | |
| 4..... | do..... | 25 | 3.4 | 9.2 | | 5.8 | 2.4 | |
| 5..... | do..... | 25 | 3.4 | 9.4 | | 6.0 | 2.4 | |
| 6..... | do..... | 25 | | | 10.4 | | | 12.8 |
| 7..... | do..... | 25 | 1.4 | 7.2 | | 5.8 | 4.4 | |
| 8..... | do..... | 10 | 2.5 | | | | 3.3 | |
| 9..... | do..... | 10 | | | 9.6 | | | 12.9 |
| 10..... | do..... | 14 | 2.0 | 8.0 | | 6.0 | 3.8 | |
| 11..... | do..... | 14 | 3.0 | 8.8 | | 5.8 | 2.8 | |
| 12..... | do..... | 19 | 2.0 | 7.8 | | 5.8 | 3.8 | |
| 13..... | do..... | 19 | 2.2 | 7.8 | | 5.6 | 3.6 | |
| 14..... | do..... | 19 | 2.0 | 8.0 | | 6.0 | 3.8 | |
| 15..... | do..... | 19 | 2.0 | 8.0 | | 6.0 | 3.8 | |
| 16..... | do..... | 27 | 2.4 | 8.0 | | 5.6 | 3.4 | |
| 17..... | do..... | 27 | 2.0 | 7.5 | | 5.5 | 3.8 | |
| 18..... | do..... | 25 | 2.2 | 8.0 | | 5.8 | 3.6 | |
| 19..... | do..... | 25 | 2.4 | 8.0 | | 5.6 | 3.4 | |
| 20..... | do..... | 25 | 2.5 | 8.3 | | 5.8 | 3.3 | |
| 21..... | do..... | 25 | 2.6 | 8.4 | | 5.8 | 3.2 | |
| 22..... | do..... | 35 | 2.4 | 8.0 | | 5.6 | 3.4 | |
| 23..... | do..... | 54 | 3.0 | 8.8 | | 5.8 | 2.8 | |
| 24..... | do..... | 75 | 2.5 | 8.4 | | 5.9 | 3.3 | |
| 25..... | do..... | 75 | 2.4 | 8.0 | | 5.6 | 3.4 | |
| 26..... | Red P..... | 380 | 3.5 | 9.5 | | 6.0 | 2.3 | |
| 27..... | do..... | 380 | 3.0 | 8.8 | | 5.8 | 2.8 | |
| 28..... | do..... | 420 | 3.5 | 9.0 | | 5.5 | 2.3 | |
| 29..... | Red and yellow P..... | 15 | 3.0 | 9.0 | | 6.0 | 2.8 | |
| 30..... | do..... | 15 | | | 10.5 | | | 13.3 |
| 31..... | do..... | 24 | 3.0 | 8.8 | | 5.8 | 2.8 | |
| 32..... | do..... | 24 | | | 10.8 | | | 13.6 |
| 33..... | do..... | 31 | 2.8 | | | | 3.0 | |
| 34..... | do..... | 31 | | | 11.0 | | | 14.0 |
| 35..... | do..... | 195 | 2.8 | 8.5 | | 5.7 | 3.0 | |
| 36..... | do..... | 195 | | | 10.5 | | | 13.5 |
| 37..... | do..... | 420 | 2.8 | 8.5 | | 5.7 | 3.0 | |
| 38..... | do..... | 380 | 3.0 | 8.8 | | 5.8 | 2.8 | |
| 39..... | do..... | 400 | 3.0 | 8.8 | | 5.8 | 2.8 | |
| 40..... | do..... | 200 | | | 10.5 | | | 12.8 |
| 41..... | do..... | 200 | 3.5 | | | | 2.3 | |
| 42..... | do..... | 130 | 3.0 | 9.0 | | 6.0 | 2.8 | |
| 43..... | do..... | 130 | | | 10.2 | | | 13.0 |

Mean resonance potential..... 5.80±0.1 volts.

Mean ionization potential..... 13.3±.5 volts.

TABLE 2.—Resonance and Ionization Potentials of Iodine

| Curve | Remarks | Tem- pera- ture | Applied potentials | | | | Resonance potential | | Initial poten- tial | Ioniza- tion poten- tial |
|---------|---------------|-----------------------|--------------------|-----|-----|-----------------------|------------------------|-----|---------------------------|-----------------------------------|
| | | | At resonance | | | At ioni- zation | | | | |
| | | | a | b | c | | | | | |
| | | °C | | | | | | | | |
| 1..... | Method 1..... | 10 | 2.0 | | | | | | 0.34 | |
| 2..... | do..... | 10 | | | | 9.5 | | | | 9.84 |
| 3..... | do..... | 10 | 2.2 | | | | | | .14 | |
| 4..... | do..... | 10 | | | | 9.5 | | | | 9.64 |
| 5..... | do..... | 10 | 2.2 | | | | | | .14 | |
| 6..... | do..... | 10 | | | | 9.5 | | | | 9.64 |
| 7..... | do..... | 15 | .7 | | | | | | 1.64 | |
| 8..... | do..... | 15 | | | | 8.8 | | | | 10.44 |
| 9..... | do..... | 10 | 1.4 | 3.8 | | | 2.4 | | .94 | |
| 10..... | do..... | 10 | | | | 9.0 | | | | 9.94 |
| 11..... | do..... | 14 | .7 | 3.2 | | | 2.5 | | 1.64 | |
| 12..... | do..... | 14 | | | | 9.0 | | | | 10.64 |
| 13..... | Method 2..... | 24 | .2 | 2.8 | 5.4 | | 2.6 | 2.6 | 2.14 | |
| 14..... | Method 1..... | 10 | 1.6 | 4.0 | | | 2.2 | | .74 | |
| 15..... | do..... | 11 | 1.8 | 4.2 | | | 2.2 | | .54 | |
| 16..... | do..... | 11 | 1.4 | 3.6 | | | 2.2 | | .94 | |
| 17..... | Method 2..... | 14 | 1.8 | 4.2 | | | 2.4 | | .54 | |
| 18..... | do..... | 14 | | | | 10.0 | | | | 10.54 |
| 19..... | Method 1..... | 0 | 1.8 | 4.0 | | | 2.2 | | .54 | |
| 20..... | do..... | 0 | | | | 9.5 | | | | 10.04 |
| 21..... | do..... | 5 | 1.6 | 3.7 | | | 2.1 | | .74 | |
| 22..... | do..... | 5 | 1.6 | 3.8 | | | 2.2 | | .74 | |
| 23..... | Method 2..... | 5 | 2.4 | 4.4 | | | 2.0 | | .06 | |
| 24..... | do..... | 10 | 1.6 | 3.8 | 6.2 | | 2.2 | 2.4 | .74 | |
| 25..... | do..... | 20 | 1.6 | 4.0 | 6.2 | | 2.4 | 2.2 | .74 | |
| 26..... | do..... | 20 | 1.0 | 3.6 | 6.2 | | 2.6 | 2.6 | 1.34 | |

Mean resonance potential..... 2.34±0.2 volts.
Mean ionization potential..... 10.1+ .5 volts.

TABLE 3.—Resonance and Ionization Potentials of Sulphur

| Curve | Remarks | Temperature | Applied potentials | | Resonance potential | Initial potential | Ionization potential |
|---------|----------------|-------------|--------------------|-----|---------------------|-------------------|----------------------|
| | | | At resonance | | | | |
| | | | a | b | b—a | | |
| | | °C | | | | | |
| 1..... | Method 1 | 128 | | | 11.5 | | 11.8 |
| 2..... | do..... | 128 | 4.5 | 9.3 | | 4.8 | 0.3 |
| 3..... | do..... | 136 | 4.0 | 8.8 | | 4.8 | .8 |
| 4..... | do..... | 136 | | | 11.0 | | 11.8 |
| 5..... | do..... | 140 | 4.5 | | | | .3 |
| 6..... | do..... | 140 | | | 11.4 | | 11.7 |
| 7..... | do..... | 169 | 4.6 | | | | .2 |
| 8..... | do..... | 169 | | | 12.2 | | 12.4 |
| 9..... | do..... | 136 | 3.5 | 8.0 | | 4.5 | 1.3 |
| 10..... | do..... | 136 | | | 12.0 | | 13.3 |
| 11..... | do..... | 136 | 3.4 | 8.0 | | 4.6 | 1.4 |
| 12..... | do..... | 142 | 3.5 | 8.0 | | 4.5 | 1.3 |
| 13..... | do..... | 142 | | | 11.5 | | 12.8 |
| 14..... | do..... | 140 | 3.6 | 8.4 | | 4.8 | 1.2 |
| 15..... | do..... | 131 | 3.8 | | | | 1 |
| 16..... | do..... | 131 | | | 11.5 | | 12.5 |
| 17..... | do..... | 149 | 3.6 | 8.2 | | 4.6 | 1.2 |
| 18..... | do..... | 171 | 3.2 | 8.0 | | 4.8 | 1.6 |
| 19..... | do..... | 171 | | | 10.5 | | 12.1 |
| 20..... | do..... | 140 | 3.6 | 8.4 | | 4.8 | 1.2 |
| 21..... | do..... | 142 | 3.6 | 8.4 | | 4.8 | 1.2 |
| 22..... | do..... | 161 | 3.4 | 8.6 | | 5.2 | 1.4 |
| 23..... | do..... | 161 | 3.2 | 8.8 | | 5.6 | 1.6 |
| 24..... | do..... | 153 | | | 11.0 | | 11.6 |
| 25..... | do..... | 153 | 4.2 | | | | .6 |
| 26..... | do..... | 120 | 3.5 | 8.0 | | 4.5 | .3 |
| 27..... | do..... | 120 | 3.6 | 8.0 | | 4.4 | 1.2 |
| 28..... | do..... | 120 | 4.4 | 9.6 | | 5.2 | .4 |
| 29..... | do..... | 120 | | | 12.0 | | 12.4 |
| 30..... | Method 2 | 140 | 4.4 | 9.0 | | 4.6 | .4 |
| 31..... | do..... | 140 | 4.3 | 9.0 | | 4.7 | .5 |

Mean resonance potential..... 4.78±0.5 volts.

Mean ionization potential..... 12.2 ± .5 volts.

TABLE 4.—Resonance and Ionization Potentials for Nitrogen

| Curve | Method | Pres- sure | Applied potentials | | | | Resonance potential | | Ioni- zation minus reso- nance poten- tials |
|---------|-------------|---------------|--------------------|------|------|-----------------------|------------------------|-----|---------------------------------------------------------------|
| | | | At resonance | | | At ioniza- tion | b-a | c-b | |
| | | | a | b | c | | | | |
| | | mm | | | | | | | |
| 1..... | 1..... | 0.75 | 8.4 | 16.4 | | | 8.0 | | |
| 2..... | 1..... | .75 | 8.4 | 16.6 | | | 8.2 | | |
| 3..... | Lenard..... | .2 | 7.4 | | | 15.5 | | | 8.1 |
| 4..... | 1..... | .2 | 8.0 | | | | | | |
| 5..... | Lenard..... | .2 | | | | 16.5 | | | 8.5 |
| 6..... | do..... | .2 | 7.8 | | | 16.5 | | | 8.7 |
| 7..... | Total..... | .2 | | | | 17.0 | | | 9.2 |
| 8..... | 1..... | .2 | 7.8 | 16.2 | | | 8.4 | | |
| 9..... | 1..... | .7 | 8.5 | 16.6 | 24.8 | | 8.1 | 8.2 | |
| 10..... | 1..... | 1.2 | 9.0 | 17.4 | | | 8.4 | | |
| 11..... | 1..... | 1.2 | 8.8 | 17.0 | 25.2 | | 8.2 | 8.2 | |
| 12..... | 1..... | 1.5 | 9.0 | 17.4 | 25.4 | | 8.4 | 8.0 | |
| 13..... | Lenard..... | 1.5 | | | | 17.0 | | | 8.0 |
| 14..... | 1..... | .1 | 8.0 | 16.2 | | | 8.2 | | |
| 15..... | Lenard..... | .1 | | | | 17.0 | | | 9.0 |
| 16..... | Total..... | .1 | | | | 16.6 | | | 8.6 |
| 17..... | Lenard..... | .1 | 7.4 | | | 16.9 | | | 8.6 |
| 18..... | 1..... | .15 | 8.4 | 16.6 | | | 8.2 | | |
| 19..... | 1..... | .7 | 8.3 | 16.6 | | | 8.3 | | |
| 20..... | Total..... | .2 | | | | 16.2 | | | 8.2 |
| 21..... | Lenard..... | .2 | 7.5 | | | 16.4 | | | 8.9 |
| 22..... | do..... | .2 | | | | 16.2 | | | 8.2 |
| 23..... | Total..... | .1 | | | | 15.5 | | | 8.5 |
| 24..... | Lenard..... | .1 | 7.0 | | | 16.0 | | | 9.0 |
| 25..... | Total..... | .1 | | | | 16.5 | | | 8.5 |
| 26..... | Lenard..... | .1 | 7.5 | | | 16.6 | | | 9.1 |
| 27..... | do..... | .2 | 7.5 | | | 16.4 | | | 8.9 |
| 28..... | do..... | .35 | 8.0 | | | 16.6 | | | 8.6 |
| 29..... | Total..... | .35 | | | | 17.8 | | | 9.0 |
| 30..... | Lenard..... | .65 | 7.8 | | | 16.5 | | | 8.7 |
| 31..... | 1..... | .8 | 8.8 | 17.2 | 25.0 | | 8.4 | 7.8 | |
| 32..... | 1..... | 1.2 | 8.2 | 16.2 | 24.0 | | 8.0 | 7.8 | |
| 33..... | 1..... | 1.1 | 7.8 | 16.0 | 24.0 | | 8.2 | 8.0 | |
| 34..... | 1..... | .85 | 7.5 | 15.5 | 24.0 | | 8.0 | 8.5 | |
| 35..... | 1..... | .85 | 7.5 | 15.5 | 24.0 | | 8.0 | 8.5 | |
| 36..... | 1..... | .85 | 7.4 | 15.6 | 23.8 | | 8.2 | 8.2 | |

Mean resonance potential.....8.18±0.1 volts.

Mean ionization potential.....8.7 + 8.18=16.9±0.5 volts.

TABLE 5.—Resonance and Ionization Potentials for Oxygen

| Curve | Method | Pres- sure | Applied potentials | | | | | Resonance potential | | | Ioni- zation minus reso- nance poten- tials |
|---------|-------------|---------------|--------------------|------|------|------|-----------------------|------------------------|-----|-----|---------------------------------------------------------------|
| | | | At resonance | | | | At ioniza- tion | b-a | c-b | d-c | |
| | | | a | b | c | d | | | | | |
| | | mm | | | | | | | | | |
| 1..... | 1..... | 0.2 | 7.2 | 15.0 | 22.5 | | | 7.8 | 7.5 | | |
| 2..... | Lenard..... | .2 | | | | | 15.0 | | | | 7.8 |
| 3..... | 1..... | .2 | 7.4 | 15.4 | 23.2 | | | 8.0 | 7.8 | | |
| 4..... | Lenard..... | .35 | | | | | 15.5 | | | | 8.3 |
| 5..... | 1..... | 1.0 | 7.2 | 15.0 | 22.5 | | | 7.8 | 7.5 | | |
| 6..... | 1..... | .45 | 6.6 | 14.8 | 22.0 | | | 8.2 | 7.8 | | |
| 7..... | Lenard..... | .45 | | | | | 14.5 | | | | 7.9 |
| 8..... | 1..... | .45 | 6.6 | 14.8 | 22.0 | | | 8.2 | 7.8 | | |
| 9..... | 1..... | .5 | 6.4 | 14.6 | 22.2 | | | 8.2 | 7.6 | | |
| 10..... | 1..... | .5 | 6.7 | 14.8 | 22.5 | | | 8.1 | 7.7 | | |
| 11..... | Lenard..... | .5 | | | | | 14.5 | | | | 7.8 |
| 12..... | do..... | .2 | | | | | 14.5 | | | | 7.7 |
| 13..... | 1..... | .2 | 6.8 | 14.8 | 23.0 | | | 8.0 | 8.2 | | |
| 14..... | 1..... | .2 | 6.7 | 14.6 | 22.4 | | | 7.9 | 7.8 | | |
| 15..... | Lenard..... | .2 | | | | | 14.2 | | | | 7.5 |
| 16..... | 1..... | .25 | 6.0 | 14.0 | 22.0 | | | 8.0 | 8.0 | | |
| 17..... | Lenard..... | .25 | | | | | 13.8 | | | | 7.8 |
| 18..... | 1..... | .6 | 6.8 | 14.6 | 22.4 | 30.2 | | 7.8 | 7.8 | 7.8 | |
| 19..... | Lenard..... | .6 | | | | | 14.2 | | | | 7.4 |
| 20..... | 1..... | .6 | 6.8 | 14.8 | 22.6 | 30.4 | | 8.0 | 7.8 | 7.8 | |
| 21..... | Lenard..... | .6 | | | | | 14.2 | | | | 7.4 |
| 22..... | 1..... | .9 | 6.4 | 14.4 | 22.4 | 30.2 | | 8.0 | 8.0 | 7.8 | |
| 23..... | Lenard..... | .9 | | | | | 14.2 | | | | 7.8 |
| 24..... | 1..... | .9 | 6.4 | 14.5 | 22.4 | 30.6 | | 7.9 | 7.9 | 8.2 | |
| 25..... | Lenard..... | .9 | | | | | 14.5 | | | | 8.1 |
| 26..... | 1..... | 1.2 | 6.6 | 14.4 | 22.4 | 30.4 | | 7.8 | 8.0 | 8.0 | |
| 27..... | Lenard..... | 1.2 | | | | | 14.2 | | | | 7.6 |
| 28..... | 1..... | .35 | 6.8 | 14.6 | 23.0 | 31.0 | | 7.8 | 8.4 | 8.0 | |
| 29..... | Lenard..... | .35 | | | | | 13.5 | | | | 6.7 |
| 30..... | 1..... | .5 | 6.6 | 14.6 | 22.5 | | | 8.0 | 7.9 | | |
| 31..... | Lenard..... | .5 | | | | | 13.8 | | | | 7.2 |

Mean resonance potential.....7.91±0.1 volts.

Mean ionization potential.....7.9 +7.6=15.5±0.5 volts.

TABLE 6.—Resonance and Ionization Potentials of Hydrogen

| Curve | Method | Pres- sure | Applied potentials at critical points | | | | | Potential difference of critical points | | | | |
|---------|-------------|---------------|---------------------------------------|------|------|------|----------------|-----------------------------------------|-----|------|-------------------|-----|
| | | | a | b | c | d | d ¹ | c-a | c-b | d-a | d ¹ -a | b-a |
| | | mm | | | | | | | | | | |
| 1..... | 1..... | 0.25 | 9.5 | | 16.0 | | | 6.5 | | | | |
| 2..... | Lenard..... | .25 | | 13.0 | 16.0 | | | | 3.0 | | | |
| 3..... | 1..... | .55 | 10.5 | | 16.5 | | | 6.0 | | | | |
| 4..... | 1..... | 1.2 | 11.0 | | | 21.8 | | | | 10.8 | | |
| 5..... | 1..... | 1.2 | 11.0 | | | 21.8 | | | | 10.8 | | |
| 6..... | 1..... | 1.2 | 11.2 | | | 21.5 | | | | 10.3 | | |
| 7..... | Lenard..... | .15 | | 12.5 | 15.5 | | | | 3.0 | | | |
| 8..... | do..... | .2 | | 12.2 | 15.4 | | | | 3.2 | | | |
| 9..... | 1..... | .2 | 9.5 | | 15.5 | | | 6.0 | | | | |
| 10..... | 1..... | .2 | 10.0 | | 15.0 | | | 5.0 | | | | |
| 11..... | Lenard..... | .2 | | 12.0 | 15.0 | | | | 3.0 | | | |
| 12..... | 1..... | .45 | 10.0 | | 15.5 | 21.2 | | 5.5 | | 11.2 | | |
| 13..... | Lenard..... | .45 | | 11.5 | 15.0 | | | | 3.5 | | | |
| 14..... | 1..... | .3 | 9.5 | | 16.0 | | | 6.5 | | | | |
| 15..... | 1..... | .3 | 9.8 | | 15.5 | | | 5.7 | | | | |
| 16..... | 1..... | .75 | 11.2 | | | 20.5 | | | | 9.3 | | |
| 17..... | 1..... | .35 | 9.6 | | 15.2 | 20.6 | | 5.6 | | 11.0 | | |
| 18..... | 1..... | .35 | 10.0 | | 15.2 | 20.5 | | 5.2 | | 10.5 | | |
| 19..... | 1..... | .35 | 10.4 | | 16.4 | 21.0 | | 6.0 | | 10.6 | | |
| 20..... | Lenard..... | .35 | | 12.0 | 15.5 | | | | 3.5 | | | |
| 21..... | 1..... | .3 | 9.4 | | 15.8 | | | 6.4 | | | | |
| 22..... | 1..... | .9 | 10.5 | | 16.0 | | | 5.5 | | | | |
| 23..... | 1..... | .3 | 9.4 | | | 19.8 | | | | 10.4 | | |
| 24..... | 1..... | .25 | 9.8 | | | 20.0 | | | | 10.2 | | |
| 25..... | 1..... | .5 | 10.4 | | 16.4 | | | 6.0 | | | | |
| 26..... | 1..... | .5 | 10.0 | | 16.2 | | | 6.2 | | | | |
| 27..... | 1..... | .5 | 11.0 | | 17.5 | 21.0 | | 6.5 | | 10.0 | | |
| 28..... | Lenard..... | .5 | | 13.0 | 16.0 | | | | 3.0 | | | |
| 29..... | do..... | .5 | 9.5 | 13.0 | | | | | | | | 3.5 |
| 30..... | do..... | .5 | 9.0 | 12.6 | | | | | | | | 3.6 |
| 31..... | do..... | .5 | | 12.8 | 15.5 | | | | 2.7 | | | |
| 32..... | 1..... | .85 | 10.0 | | 16.0 | | | 6.0 | | | | |
| 33..... | 1..... | .85 | 9.6 | | 15.8 | | | 6.2 | | | | |
| 34..... | Lenard..... | .85 | 9.5 | 12.4 | | | | | | | | 2.9 |
| 35..... | 1..... | .35 | 9.5 | | 16.0 | | | 6.5 | | | | |
| 36..... | 1..... | .35 | 9.5 | | 15.5 | | | 6.0 | | | | |
| 37..... | 1..... | .35 | 9.5 | | | 21.5 | | | | | 12.0 | |
| 38..... | 1..... | .5 | 10.0 | | 20.5 | | | | | 10.5 | | |
| 39..... | 1..... | .5 | 8.5 | | 15.0 | | | 6.5 | | | | |
| 40..... | 1..... | .35 | 10.0 | | | 19.6 | | | | 9.6 | | |
| 41..... | 1..... | .35 | 10.0 | | 16.5 | | | 6.5 | | | | |
| 42..... | 1..... | .40 | 12.0 | | 17.5 | 23.0 | | 5.5 | | 11.0 | | |
| 43..... | 1..... | .40 | 12.0 | | 18.2 | | | 6.2 | | | | |
| 44..... | Lenard..... | .40 | | 14.4 | 17.6 | | | | 3.2 | | | |
| 45..... | 1..... | .45 | 11.5 | | 18.0 | 22.0 | | 6.5 | | 10.5 | | |
| 46..... | 1..... | .45 | 10.5 | | 17.5 | | | 7.0 | | | | |
| 47..... | 1..... | .45 | 9.0 | | 15.0 | | 22.0 | 6.0 | | | 13.0 | |
| 48..... | 1..... | .9 | 9.0 | | 15.0 | | | 6.0 | | | | |
| 49..... | Lenard..... | .9 | | 11.8 | 15.5 | | | | 3.7 | | | |
| 50..... | 1..... | .9 | 8.5 | | 15.2 | | | 6.7 | | | | |
| 51..... | 1..... | .9 | 8.5 | | 15.0 | | | 6.5 | | | | |
| 52..... | 1..... | .7 | 9.0 | | 16.0 | | | 7.0 | | | | |
| 53..... | Lenard..... | .3 | | 13.0 | 16.5 | | | | 3.5 | | | |

TABLE 6.—Resonance and Ionization Potentials of Hydrogen—Continued

| Curve | Method | Pres- sure | Applied potentials at critical points | | | | | Potential difference of critical points | | | | |
|------------|------------|---------------|---------------------------------------|------|------|------|----------------|-----------------------------------------|------|-------|-------------------|-----|
| | | | a | b | c | d | d ¹ | c-a | c-b | d-a | d ¹ -a | b-a |
| 54..... | 1..... | .3 | | 12.5 | 16.2 | | | | 3.7 | | | |
| 55..... | 1..... | .7 | 11.0 | | 17.0 | 21.5 | | 6.0 | | 10.5 | | |
| 56..... | 1..... | .7 | 10.5 | | 16.8 | 21.0 | | 6.3 | | 10.5 | | |
| 57..... | Lenard.... | .7 | | 13.5 | 17.0 | | | | 3.5 | | | |
| 58..... | 1..... | .4 | 10.5 | | | | 22.5 | | | | 12.0 | |
| 59..... | 1..... | .8 | 9.0 | | | | 21.0 | | | | 12.0 | |
| 60..... | 1..... | .4 | 9.5 | | | 20.5 | | | | 11.0 | | |
| 61..... | 1..... | 1.0 | 10.0 | | 15.5 | | 20.5 | 5.5 | | 10.5 | | |
| 62..... | 1..... | 1.0 | 9.0 | | | | 21.0 | | | | 12.0 | |
| 63..... | 1..... | .5 | 10.5 | | 16.5 | | | 6.0 | | | | |
| 64..... | 1..... | .3 | 10.6 | | | 20.8 | | | | 10.2 | | |
| 65..... | 1..... | .45 | 11.5 | | 17.5 | 22.0 | | 6.0 | | 10.5 | | |
| 66..... | 1..... | .33 | 11.4 | | | 21.0 | | | | 9.6 | | |
| 67..... | 1..... | .28 | 10.0 | | | 20.0 | | | | 10.0 | | |
| 68..... | 1..... | .30 | 11.0 | | | 21.5 | | | | 10.5 | | |
| 69..... | 1..... | .45 | 11.5 | | | 22.0 | | | | 10.5 | | |
| 70..... | 1..... | .40 | 11.0 | | 17.5 | 21.0 | | 6.5 | | 10.0 | | |
| 71..... | 1..... | .35 | 11.5 | | 17.5 | | | 6.0 | | | | |
| Means..... | | | | | | | | 6.11 | 3.24 | 10.40 | 12.2 | 3.3 |

a=First resonance.

b=First ionization.

c=Second ionization.

d=First resonance repeated.

d¹=Two successive collisions of first resonance and second resonance type.c-a=Second ionization potential minus first resonance potential giving second ionization potential $10.40+6.11=16.51\pm0.5$ volts.c-b=Second ionization potential minus first ionization potential giving first ionization potential $16.51-3.24=13.27\pm0.5$ volts.d-a=First resonance potential 10.40 ± 0.5 volts.d¹-a=Second resonance potential 12.2 volts—(doubtful).b-a=First ionization potential minus first resonance potential giving first ionization potential $10.40+3.3=13.7$ volts—(doubtful).

TABLE 7.—Summary of Critical Potentials of Gases and Vapors

| Element | Resonance | | | Ionization | | |
|-----------------|-----------|------------------|------------------------------------------------------------------|------------|------------------|----------------|
| | Observed | Theo- retical | Wave length | Observed | Theo- retical | Wave length |
| | | | λ in A | | | λ in A |
| Phosphorus..... | 5.80 | | 2130 | 13.3 | | 928 |
| Iodine..... | 2.34 | | 5300 | 10.1 | | 1220 |
| Sulphur..... | 4.78 | | 2580 | 12.2 | | 1010 |
| Nitrogen..... | 8.18 | 8.270 | $\left\{ \begin{array}{l} 1492.8 \\ 1494.8 \end{array} \right\}$ | 16.9 | | 730 |
| Oxygen..... | 7.91 | | 1560 | 15.5 | | 796 |
| Hydrogen..... | 10.40 | 10.16 | 1215.6 | 13.3 | 13.54 | 911.78 |
| | 12.22 | | | 16.5 | 16.26 | |

Italicized wave lengths are computed from observed potentials. The others are spectroscopic values from which theoretical potentials have been computed.

